DESCRIPTION

# METHOD AND APPARATUS FOR MODIFYING OBJECT WITH ELECTRONS GENERATED FROM COLD CATHODE ELECTRON EMITTER

## TECHNICAL FIELD

The present invention relates to method and apparatus for modifying an object with electrons.

## BACKGROUND ART

In the past, electron irradiation has been utilized to surface modify, sterilize or clean an object. For example, Japanese Patent Early Publication [kokai] No. 2002-6094 discloses an electron irradiating apparatus that can be used to form a cross-bridge structure or purify exhaust gas. This apparatus is provided with an electron gun having a hot filament, high-voltage power source for supplying an electric current to the hot filament to generate electrons, accelerating electrode for accelerating the generated electrons to obtain an electron beam, and an electromagnet for deflecting the electron beam.

However, since the hot filament is an electron source having a spot-like or linear electron emitting portion, it is needed to scan the electron beam to modify a relatively wide surface area of the object. This leads to a reduction in treatment efficiency, and a complication in device structure. In addition, since the hot filament is heated under a high degree of vacuum to generate the electrons, vacuum equipments such as decompression chamber and vacuum pump are needed. As a result, there is a problem that the application area of the apparatus is narrow despite an increase in cost of the apparatus.

On the other hand, Japanese Patent Early Publication No. 3-29662 discloses a method of sterilizing animal feeding stuff by irradiation of a high energy electron beam of 5 to 10 MeV. In addition, Japanese Patent Early Publication No. 2000-69908 discloses a method of sterilizing green tea powder by irradiation of an electron bean of 200 keV to 300 keV. In these methods, since an expensive electron accelerator is needed to obtain the high energy electron beam, a considerable increase in cost of the apparatus becomes a

problem. In addition, it has been difficult to irradiate such a high electron beam to a wide surface area of the object at a time.

SUNNARY OF THE INVENTION

In view of the above-mentioned problems, a concern of the present invention is to provide a method of efficiently and uniformly modifying an object with electrons even when the object has a relatively wide surface area to be modified.

That is, the method of the present invention comprises the steps of providing a cold-cathode electron emitter, which has the capability of emitting electrons from a planar electron emitting portion according to tunnel effect, applying a voltage to the emitter to emit the electrons from the planar electron emitting portion, and exposing the object to the emitted electrons. As the cold-cathode electron emitter, it is particularly preferred to use a Ballistic electron Surface-emitting Device (BSD) comprising a pair of electrodes, and a strong field drift layer including nanocrystalline silicon disposed between the electrodes.

According to the present invention, since the cold cathode electron emitter that is a planar-type electron emitting source is used, it is possible to perform the modifying treatment to the object under a reduced pressure near atmospheric pressure in addition to the improvement in treatment efficiency and uniformity. In particular, when using the BSD as the cold cathode electron emitter, it is possible to perform the modifying treatment under the atmospheric pressure without using vacuum equipments such as a vacuum pump and decompression chamber. Therefore, there are many advantages of an expansion of the application area, downsizing of the apparatus, and a reduction in cost of the modifying treatment.

In the present invention, the meaning of the word “modify” or “modifying” includes various types of reactions such as hardening, polymerization, decomposition, bridging, oxidizing, ionization, excitation and radical reaction, changing surface tension, surface energy, wettability, adhesion, absorption

index, refractive index or crystal structure, introduction of defects, sterilization, disinfection, filtration of virus, mold, pollen and so on, physiological actions such as germination, ageing or prevention maturation, propagation of good bacteria, deodorizing, cleaning, purifying, and removal of harmful substances.

In the above method, it is preferred that an energy of the electrons used to modify the object is selected from a range of 1 eV to 50 keV, and preferably 1～100 eV.

A further concern of the present invention is to provide an apparatus for efficiently and uniformly modifying an object with electrons. That is, this apparatus comprises a cold-cathode electron emitter, which has the capability of emitting electrons from a planar electron emitting portion according to tunnel effect, voltage applying unit for applying a voltage to the emitter to emit the electrons from the planar electron emitting portion, and a case for accommodating the emitter therein. The case has an opening, through which the electrons or a gas activated by the electrons are provided. From the same reason as the above, it is particularly preferred to use a Ballistic electron Surface-emitting Device (BSD) as the cold-cathode electron emitter, which comprises a pair of first and second electrodes, and a strong field drift layer including nanocrystalline silicon disposed between the first and second electrodes.

In addition, it is preferred that the above apparatus further comprises an accelerating electrode positioned in face-to-face relation with the planar electron emitting portion to accelerate the electrons. In this case, it is possible to control the energy of electrons irradiated to the object.

In the above apparatus, it is preferred that the first electrode is composed of an array of first electrode strips, which are arranged to be spaced from each other in a lateral direction, and the second electrode is composed of an array of second electrode strips, which are arranged to be spaced from each other in a direction intersecting with the lateral direction, wherein the electrons are selectively emitted from the planar electron emitting portion corresponding to

an intersecting region(s) between at least one of the first electrode strips and at least one of the second electrode strips when the voltage is applied therebetween by the voltage applying unit. Furthermore, it is preferred that the apparatus has an first selector for selecting at least one of the first electrode strips, and a second selector for selecting at least one of the second electrode strips, wherein the voltage applying unit applies the voltage between at least one of the first electrode strips selected by the first selector and at least one of the second electrode strips selected by the second selector to selectively emit the electrons from the planar electron emitting portion corresponding to the intersecting region(s) therebetween. In this case, it is possible to change a modification area depending on the size of the object, thereby achieving energy saving and reducing the modification cost.

Another concern of the present invention is to provide an apparatus for performing the modifying method described above. This apparatus comprises a cold-cathode electron emitter, which has the capability of emitting electrons from a planar electron emitting portion according to tunnel effect, voltage applying unit for applying a voltage to the emitter to emit the electrons from the planar electron emitting portion, and a holder for supporting the object such that the object is exposed to the emitted electrons. From the same reason as the above, it is particularly preferred to use the BSD as the cold-cathode electron emitter.

These and still other objects and advantages of the present invention will become more apparent from the best mode for carrying out the invention, referring to the attached drawings.

## BRIEF EXPLANATION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of an apparatus for modifying an object with electrons according to a first embodiment of the present invention;

FIG. 2 is a schematic perspective view of a cold cathode electron emitter of the apparatus;

FIG. 3 is a schematic perspective view of another cold cathode electron emitter;

FIG. 4 is an explanatory view of a strong-field drift layer of the cold cathode electron emitter;

FIG. 5 is a graph showing energy distributions of electrons emitted from the cold cathode electron emitter;

FIG. 6 is a schematic cross-sectional view of an apparatus according to a modification of the first embodiment;

FIGS. 7A and 7B are schematic perspective views of preferred arrangements of cold cathode electron emitters;

FIG. 8 is a schematic cross-sectional view of an apparatus according to a further modification of the first embodiment;

FIG. 9 is a schematic cross-sectional view of an apparatus according to another modification of the first embodiment;

FIG. 10 is a schematic cross-sectional view of an apparatus for modifying an object with electrons according to a second embodiment of the present invention;

FIG. 11 is a schematic cross-sectional view of an apparatus according to a first modification of the second embodiment;

FIG. 12 is a schematic cross-sectional view of an apparatus according to a second modification of the second embodiment;

FIG. 13 is a schematic cross-sectional view of an apparatus according to a third modification of the second embodiment;

FIG. 14 is a schematic cross-sectional view of an apparatus according to a fourth modification of the second embodiment;

FIG. 15 is a schematic cross-sectional view of an apparatus for modifying a gas object with electrons according to a third embodiment of the present invention;

FIG. 16 is a schematic cross-sectional view of an apparatus for modifying a liquid object according to a modification of the third embodiment;

FIG. 17 is a schematic cross-sectional view of an apparatus for modifying a sold object according to a further modification of the third embodiment;

FIGS. 18A and 18B are top and cross-sectional views of an apparatus for modifying an object with electrons according to a fourth embodiment of the present invention;

FIG. 19 is a schematic cross-sectional view showing a method of modifying an object with electrons according to a fifth embodiment of the present invention; and

FIG. 20 is a schematic cross-sectional view showing a modifying treatment according to a modification of the fifth embodiment.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is explained below in detail according to preferred embodiments.

(FIRST EMBODIMENT)

As shown in FIGS. 1 and 2, an apparatus for modifying an object **2** with electrons according to the present embodiment comprises a cold cathode electron emitter **1** having a planar electron emitting portion **10**, a voltage applying unit **30** for applying a voltage to the emitter to emit electrons from the planar electron emitting portion, a case **20** for accommodating the emitter therein, which is made of an insulating material and has an opening **21** used to provide the emitted electrons to the outside of the case, and a holder **40** for supporting the object **2** such that the object is exposed to the electrons provided through the opening. In FIG. 1, the numeral **50** designates a mesh electrode attached to the opening **21** to accelerate the electrons generated from the emitter **1**. Alternatively, a window member made of a material, through which the electrons can pass, may be attached to the opening in place of the accelerating electrode.

As shown in FIG. 2, the cold cathode electron emitter **1** comprises a conductive substrate **14** such as n-type silicon, a non-doped polycrystalline silicon layer **13** formed on a top surface of the conductive substrate **14**, strong-field drift layer **12** formed on the polycrystalline silicon layer **13**, a first electrode **11** provided on the strong-field drift layer **12**, and an ohmic electrode

**15** formed on the bottom surface of the conductive substrate **14**. In this case, the conductive substrate **14** and the ohmic electrode **15** function as a second electrode. In addition, a top surface of the first electrode **11** provides the planar electron emitting portion **10** of the emitter **1**. The strong-field drift layer **12** may be directly formed on the conductive substrate not through the polycrystalline silicon layer **13**. Alternatively, another cold cathode electron emitter **1** shown in FIG. 3 may be used, which is characterized in that an insulating substrate **16** such as glass or a ceramic material is used in place of the conductive substrate **14**, an electrode layer **17** is formed as the second electrode on the insulating substrate, and the strong-field drift layer **12** is formed on the electrode layer **17**. The cold cathode electron emitter **1** used in this embodiment is known as Ballistic electron Surface-emitting Device (BSD).

As shown in FIG. 4, the strong field drift layer **12** is composed of columnar polycrystalline silicon grains **100** extending toward the first electrode **11**, first silicon oxide thin films **110** formed in surfaces of the silicon grains **100**, fine grains of nanocrystalline silicon **120** formed between the adjacent silicon grains **110**, and second silicon oxide thin films **130** formed in surfaces of the fine grains **120**, each of which has a smaller thickness than a crystal grain size of the nanocrystalline silicon.

For example, the strong field drift layer **12** can be produced according to the following procedures. Firstly, a nanocrystallization process is performed to a non-doped polycrystalline silicon layer on a conductive substrate , thereby obtaining a nanocrystalline composite layer having the columnar polycrystalline silicon grains **100** and the fine grains of nanocrystalline silicon **120**. In the nanocrystallization process, for example, an electrolytic solution obtained by mixing a 55 wt% hydrofluoric aqueous solution with ethanol at a mixing ratio of 1 : 1 is used.

Then, the conductive substrate having an electrode layer used as the ohmic electrode and the polycrystalline silicon layer is placed in the electrolytic solution. The electrode layer is used as anode electrode, and a platinum

electrode positioned on the polycrystalline silicon layer is used as cathode electrode. By supplying a constant electric current having a current density of 12 mA/cm$^2$ between the anode and cathode electrodes for a predetermined time period, e.g., 10 seconds, while irradiating light from a 500 W tungsten lamp, the nanocrystalline composite layer can be obtained. In the nanocrystalline composite layer, amorphous silicon may be formed at regions other than the silicon grains **100** and the fine grains of nanocrystalline silicon **120**. Alternatively, depending on the condition of the nanocrystalline process, the amorphous silicon regions may be formed by fine pores. In this case, the nanocrystalline composite layer has a porous structure.

Next, an oxidizing process is performed to the nanocrystalline composite layer to obtain the strong field drift layer **12**. In this oxidizing process, for example, an electrolytic solution obtained by adding 0.04 mol/l of potassium nitrate into an organic solvent such as ethyleneglycol is used. Then, the conductive substrate having the nanocrystalline composite layer is placed in the electrolytic solution. The electrode layer used as the ohmic electrode is the anode electrode, and a platinum electrode positioned on the nanocrystalline composite layer is used as cathode electrode. By supplying a constant electric current having a current density of 0.1 mA/cm$^2$ between the anode and cathode electrodes for a time period needed for a voltage increase of 20 V therebetween, the nanocrystalline composite layer can be electrochemically oxidized to obtain the strong field drift layer **12**.

In the strong field drift layer **12**, amorphous silicon or a partially-oxidized amorphous silicon may be formed at regions other than the silicon grains **100**, the fine grains of nanocrystalline silicon **120**, the first and second silicon oxide thin films (**110**, **130**). When forming these silicon oxide thin films (**110**, **130**), a nitriding process or an oxynitriding process may be performed in place of the oxidizing process described above. In the case of the nitriding process, those silicon oxide thin films are replaced by silicon nitride thin films. In the case of the oxynitriding process, those silicon oxide thin films are replaced by silicon

oxynitride thin films.

To emit electrons from the cold cathode electron emitter **1**, when a required voltage is applied between the first electrode **11** and the ohmic electrode **15** such that an electric potential of the first electrode is higher than the electric potential of the ohmic electrode, electrons are injected from the second electrode into the strong field drift layer **12**. At this time, since most of the electric field is impressed to the first and second silicon oxide thin films (**110**, **130**) of the strong field drift layer **12**, the injected electrons are accelerated by the strong electric field impressed to those silicon oxide thin films, so that the electrons are drifted in regions between the silicon grains **100** of the strong field drift layer **12**, as shown by the arrows in FIG. 4, and emitted outside through the first electrode **11** without being almost scattered by the fine grains of nanocrystalline silicon **120**. This phenomenon is called as Ballistic electron Surface-emitting phenomenon that is a kind of the tunnel effect. Since heat generated from the strong field drift layer **12** is released through the silicon grains **100**, it is possible to avoid the occurrence of popping at the time of the electron emission.

Electrons emitted from the cold cathode electron emitter **1** is called as cold electrons. On the contrary, electrons generated from a spot-like or linear electron emitter such as hot filament by heating is called as thermal electrons. In addition, the cold cathode electron emitter 1 used in the present invention is known as an field-emission type electron source that is preferably used for display devices, for example, as disclosed in Japanese Patent Early Publication No. 2000-100316.

The electrons provided from the cold cathode electron emitter **1** through the opening **21** of the case **20** are irradiated to a surface to be modified of the object **2** supported by the holder **40**. An energy of the electrons irradiated can be determined according to the purpose of the modifying treatment. For example, to avoid radio activation of the object, it is preferred to use the energy less than 10 MeV, and more preferably less than 1 MeV. In the case of using

the energy smaller than 300 keV, a radiological protection equipment for X-ray can be simplified.

To achieve desired modifying effects that meet the purpose of the present invention, it is preferred to use electrons having an energy selected from a range of 1 to 50 keV, and particularly 1 to 100 eV. When irradiating the electrons having the energy of approximately 4 eV, atoms and molecules can be excited. In addition, when irradiating the electrons having an energy of 4 to 12 eV, which is equal to or slightly larger than 4 to 8 eV of the bonding energy between atoms, the object can be effectively surface modified. When irradiating the electrons having an energy of 20 to 100 eV, atoms and molecules can be ionized. Furthermore, when irradiating the electrons having an energy smaller than the ionization energy to a gas containing moisture or steam as the object, the electrons are attached to the object, so that minus ions can be readily generated.

By the way, there is an advantage that the energy level of the electrons emitted from the cold cathode electron emitter is higher in proportion to a magnitude of the voltage applied between the electrodes. For example, electrons having an energy of 1 eV to several ten electron volts can be obtained by use of 10 to 20 V of the applied voltage, which is much higher than the electron level, e.g., 0.1 eV, of the thermal electrons generated from the hot filament.

As an example, energy distributions of electrons emitted from the cold cathode electron emitter **1** are shown in FIG. 5. In this figure, "A", "B" and "C" designate profiles showing the energy distributions obtained when the voltages of 12 V, 14V and 16V are respectively applied between the electrodes. These profiles show that as the applied voltage increases, the peak becomes sharper, and the peak position is shifted to the high energy side.

In the case of controlling the energy of the electrons emitted from the cold cathode electron emitter **1**, it is preferred to dispose an accelerating electrode **50** above the first electrode **11** in the vicinity of the opening **21** of the case **20**,

and apply a required voltage between the accelerating electrode and the first electrode such that an electric potential of the accelerating electrode is higher than the electric potential of the first electrode. For example, as shown in FIG. 3, when a voltage **Vps** is applied between the first and second electrodes (**11**, **17**) of the cold cathode electron emitter **1**, and an acceleration voltage **Vc** is applied between the accelerating electrode (anode electrode) **50** and the first electrode **11** such that the electric potential of the accelerating electrode is higher than the electric potential of the first electrode, it is possible to control the energy of the emitted electrons depending on a magnitude of the acceleration voltage **Vc**.

In FIG. 3, when an electric current flowing between the first and second electrodes (**11**, **17**) is represented as a diode current **Ips**, and an electric current flowing between the accelerating electrode **50** and the first electrode **11** is represented as an emission current **Ie**, an electron emissivity can be defined as a rate of the emission current **Ie** to the diode current **Ips** (=**Ie/Ips**). As this ratio is larger, the electron emissivity increases. According to the present invention, even when a relatively low voltage of 10 to 20 V is applied as the voltage **Vps** between the first and second electrodes (**11**, **17**), it is possible to emit the electrons. In addition, since the dependence of the electron emissivity on degree of vacuum is small, and popping does not happen at the time of electron emission, it is possible to stably emit the electrons at an improved electron emissivity. This means that electrons can be emitted at a pressure in the vicinity of atmospheric pressure. As the voltage **Vps**, a constant DC voltage or a pulse voltage can be used. In the case of using the pulse voltage, a reverse-bias voltage may be applied when the voltage **Vps** is not applied. Similarly, as the acceleration voltage **Vc**, a constant DC voltage or a pulse voltage can be used.

The accelerating electrode **50** can be made of a metal material such as aluminum, tungsten and stainless steel. In addition, the accelerating electrode **50** may be configured in a frame shape to fit the opening **21** of the case **20**. In

this case, the electrons are irradiated to the object through an inner space of the frame shape of the accelerating electrode. Alternatively, a grid electrode may be disposed in the vicinity of the opening of the case.

In conclusion, the modifying apparatus and method of this embodiment presents the following effects.

(1) Since the cold cathode electron emitter having the planar electron emitting portion is used, it is possible to uniformly irradiate electrons to a wide surface area of the object at a time, as compared with the case of using an electron emitting source having a spot-like or linear electron emitting portion such as hot filament. As a result, improved modification efficiency and uniformity can be achieved.

(2) The cold cathode electron emitter such as BSD has the capability of emitting electrons under atmospheric pressure. Therefore, it is possible to perform the modifying treatment without using vacuum equipments such as decompression chamber and vacuum pump.

(3) The cold cathode electron emitter can be driven by a pulse voltage because a rise time needed to emit the electrons is shorter than the electron emitting source for emitting thermal electrons such as hot filament. Therefore, there is an advantage of saving power consumption.

(4) Since no device for scanning the electron beam is needed in the present invention, a reduction in cost of the apparatus can be achieved.

As a modification of this embodiment, as shown in FIG. 6, it is preferred that a pair of cold-cathode electron emitters **1**, each of which is the cold-cathode electron emitter explained above, are disposed such that electrons are emitted in opposite two directions through a pair of openings **21** formed in the case **20**. In this case, the second electrodes **17** of the pair of cold-cathode electron emitters are respectively connected to opposite surfaces of the insulating substrate **16**, as shown in FIG. 7A Alternatively, it is preferred that the ohmic electrodes **15** of the pair of cold-cathode electron emitters are composed of a common electrode disposed between strong field drift layers **12**,

as shown in FIG. 7B In this case, electrons are emitted in opposite two directions by applying a voltage between the common electrode **15** and the first electrodes **11** of the cold-cathode electron emitters. Therefore, it is possible to simplify the voltage applying unit by reducing the number of electrodes.

In addition, by forming a two or three dimensional array of at least one cold cathode electron emitter having the capability of simultaneously emitting the electrons in the opposite two directions, as shown in FIG. 7A or 7B, and at least one cold cathode electron emitter having the capability of emitting the electrons in one direction, as shown in FIG. 2 or 3, it is possible to design a high-efficiency modifying apparatus for simultaneously irradiating electrons to the object from different directions. For example, a modifying apparatus shown in FIG. 8 has a pair of treatment spaces, in each of which electrons can be simultaneously irradiated from the opposite two directions. In FIG. 8, the numeral **72** designates a gas supply unit for supplying a gas as the object into the case. Therefore, the gas activated by the electrons in the treatment spaces is ejected outside through the opening **21** of the case **20**.

A modifying apparatus according to a modification of this embodiment is shown in FIG. 9. This apparatus is characterized by comprising a holder **40** for supporting the object **2**, and an emitter traveling unit **60** for traveling the case **20** with the cold cathode electron emitter **1** therein around the object. As the emitter traveling unit, for example, it is preferred that a rail **61** is formed along a desired trajectory, and a carrier **63** for the case **20** is traveled along the rail. In this case, it is possible to selectively irradiate the electrons to a desired surface area of the object, without moving the object, and also change the irradiation angle of the electrons to the object.

The emitter traveling unit **60** may further comprise a distance adjuster for moving the case **20** upward or downward against the carrier **63** to adjust the distance between the cold cathode electron emitter **1** and the object **2**. In addition, the holder **40** may be rotatable around the holder axis, if necessary. When it is needed to perform the modifying treatment in a desired gas

atmosphere, it is preferred that the above-described modifying apparatus is accommodated in a chamber with a gas supply unit for charging the gas into the chamber. In the present invention, since the modifying treatment can be performed under atmospheric pressure, the structure of the chamber can be simplified as compared with the case of forming a decompression chamber. The emitter traveling unit **60** and the gas supply unit can be controlled by use of an operation panel provided outside of the chamber.

(SECOND EMBODIMENT)

In this embodiment, apparatus and method for modifying a gas as the object by irradiation of electrons are explained.

As shown in FIG. 10, the modifying apparatus of this embodiment is characterized by comprising a case **20** having a gas inlet **22** for supplying the object gas into the case, and an opening **21** for providing a modified gas to the outside, and an acceleration electrode (anode electrode) **50** disposed in a face-to-face manner with an electron emitting portion **10** of a cold cathode electron emitter **1** in the case. The cold cathode electron emitter is the same as the emitter used in the first embodiment. Therefore, duplicate explanation is omitted. To avoid the influence of humidity on electron emitting efficiency of the cold cathode electron emitter, it is preferred that the gas supplied in the case **20** through the gas inlet **22** is a dry gas having a low moisture content. For example, it is preferred that the relative humidity (RH%) is smaller than 30%, and more preferably 10%. In the case, electrons emitted from the cold cathode electron emitter **1** are accelerated toward the acceleration electrode **50**, and irradiated to the gas existing in a space between the cold cathode electron emitter and the acceleration electrode to ionize the gas. As a result, the ionized gas is provided outside through the opening **21**.

For example, negative ions can be readily generated by supplying the dry gas containing an element having positive electron affinity or a large electron affinity such as oxygen in the case **20** through the gas inlet **21**. In this case, it is preferred to apply an acceleration voltage **Vc** of several volts to several ten

volts between the acceleration electrode **50** and the first electrode **11**. The generated negative ions provided through the opening **21** are bonded with molecules in the outside air to generate various sorts of ions. On the other hand, when a voltage of several ten volts to several mega volts, which is larger than the ionization energy (for example, several ten electron volts) of the dry gas, is applied between the acceleration electrode **50** and the first electrode **11**, positive ions can be generated.

It is also preferred that an auxiliary electrode (not shown) is placed outside of the case **20** in front of the opening **21** to control the amounts of ions ejected therefrom. In the case of ejecting the negative ions from the opening **21**, it is preferred that an electric potential of the auxiliary electrode is determined to be higher than the electric potential of the first electrode **11** of the cold cathode electron emitter **1**. In addition, as shown in FIG. 11, a pair of auxiliary electrodes (**55, 56**) may be disposed in the case **20** such that one of the auxiliary electrodes **55** is positioned adjacent to the cold cathode electron emitter **1** and at the side of the opening **21**, and the other auxiliary electrode **56** is positioned adjacent to the acceleration electrode **50** at the side of the opening. In this case, it is preferred that an electric potential of the auxiliary electrodes (**55, 56**) is determined to be higher than the first electrode **11** of the cold cathode electron emitter **1** to eject the negative ions from the opening **21**.

The structure of the auxiliary electrode is not specifically limited. For example, the auxiliary electrode comprises a mesh electrode, grid electrode, electrode obtained by concentrically arranging ring-like electrode members having different diameters, and an electrode obtained by arranging a plurality of linear electrode members in parallel with each other. In addition, the modifying apparatus may comprise a spray unit for spraying a second gas containing liquid particles such as medical constituents or steam to the ions ejected through the opening **21** of the case **20**. In this case, the second gas can be ionized by the ions provided from the case.

A modifying apparatus according to a modification of this embodiment is

shown in FIG. 12. This apparatus is characterized by using a case **20** having air inlets **22** for supplying a low moisture gas such as dried air, oxygen or an inert gas in the case, which are formed in opposite side walls of the case, and an opening **21** for ejecting the electrons emitted from the cold cathode electron emitter **1** and the gas modified by the electrons, which is formed in a top wall of the case **20** and above the electron emitting portion **10** of the cold cathode electron emitter **1**.

To control the energy of the electrons ejected from the opening **21**, as shown in FIG. 13, an acceleration electrode (anode electrode) **50** having a ring shape can be disposed above the opening of the case **20**. If necessary, an auxiliary electrode **55** such as mesh electrode may be attached to an inner surface of the top wall of the case **20** around the opening **21**. In this case, it is preferred that an electric potential of the auxiliary electrode **55** is determined to be higher than the electric potential of the first electrode **11** of the cold cathode electron emitter **1**, and the electric potential of the accelerating electrode **50** is determined to be higher than the electric potential of the auxiliary electrode **55**. The electrons emitted from the cold cathode electron emitter **1** are accelerated by the accelerating electrode **50** and the auxiliary electrode **55**, and then irradiated to the object **2** supported by the holder **40** through a center opening of the accelerating electrode.

Alternatively, the auxiliary electrode **55**, e.g., mesh electrode may be disposed between the electron emitting portion **10** of the cold cathode electron emitter **1** and the accelerating electrode **50** attached to an inner surface of the top wall of the case **20**, as shown in FIG. 14. In this case, a gas supplied from gas inlets **22** in the case **20** is modified by electrons emitted from the cold cathode electron emitter **1**, and then the modified gas is ejected outside from a pair of openings **21** formed in upper portions of opposite side walls of the case **20**.

(THIRD EMBODIMENT)

In this embodiment, modifying apparatus and method for irradiating

electrons to a gas or a gas containing liquid particles such as steam or moisture are explained.

That is, as shown in FIG. 15, this modifying apparatus is characterized by using a case **20** comprising gas inlets **22** for supplying a gas into the case, which are formed in lower portions of side walls of the case, and an opening **21** for ejecting electrons emitted from the cold cathode electron emitter **1**, which is formed in a top wall at a position facing the electron emitting portion **10** of the cold cathode electron emitter placed on a bottom wall of the case. In addition, this apparatus has an accelerating electrode **50** disposed above the opening, and a gas flow channel **70** provided on the top wall of the case **20**. In this case, the gas is supplied as the object to the gas flow channel **70** from a gas supply unit **72**, as shown by the horizontal arrow in FIG. 15, and then modified by the electrons accelerated from the cold cathode electron emitter **1** toward the acceleration electrode **50** through the opening **21**. In addition, an auxiliary electrode **55** configured in a ring shape is attached to the inner surface of the top wall of the case around the opening **21**. It is preferred that an electric potential of the auxiliary electrode **55** is determined to be higher than the electric potential of the first electrode **11** of the cold cathode electron emitter **1**, and an electric potential of the accelerating electrode **50** is determined to be higher than the electric potential of the auxiliary electrode **55**.

In this embodiment, it is preferred that the gas supplied in the case **20** through the gas inlet **22** is a gas composed of atoms or molecules having a smaller electron affinity than oxygen. For example, such a gas comprises helium, argon, xenon, and nitrogen. In this case, the electron emitted from the cold cathode electron emitter **1** can be efficiently provided to the gas flowing in the gas flow channel **70** . In other words, when the air is charged in the case **20**, the number of electrons having a sufficient energy for achieving the purpose of the modifying treatment may decrease, or variations in energy distribution of the electrons may increase because of interference of the electrons emitted from the cold cathode electron emitter with atoms and

molecules in the air. Due to this reason, when the air is charged in the case, it is preferred that the gas flow channel **70** is spaced from the electron emitting portion **10** of the cold cathode electron emitter **1** by a distance of 5 mm to 1 cm to perform the modifying treatment.

On the other hand, when the gas having a smaller electron affinity than oxygen is charged in the case **20**, the gas flow channel **70** can be spaced from the electron emitting portion **10** by a larger distance of several cm to several ten cm. As a result, it leads to an improvement in modifying efficiency and a higher degree of freedom of designing the apparatus. In addition, it is possible to prevent contamination of the cold cathode electron emitter **1**, and prolong the maintenance cycle. The gas supplied into the gas flow channel **70** may contain medical constituents as the liquid particles.

As a modification of this embodiment, in the case of irradiating electrons to a liquid as the object, it is preferred that the cold cathode electron emitter **1** is disposed on the inner surface of the top wall of the case **20**, and electrons emitted downwardly from the cold cathode electron emitter are irradiated to the liquid through the opening **21** formed in the bottom wall of the case, as shown in FIG. 16. In FIG. 16, the numeral **80** designates a liquid flow channel disposed under the case **20**. The liquid is supplied to the liquid flow channel **80** by a liquid supply unit **82**. In addition, by replacing the liquid flow channel **80** with a conveyer **90** such as a belt conveyer, as shown in FIG. 17, it is possible to successively modify solid objects on the conveyer **90** by the irradiation of electrons.

(FOURTH EMBODIMENT)

In this embodiment, a modifying apparatus having the capability of changing an electron irradiation area depending on the size of the object is explained. That is, as shown in FIGS. 18A and 18B, the first electrode **11** of the cold cathode electron emitter **1** is composed of an array of first electrode strips **X1** to **X8**, which are arranged to be spaced from each other in a lateral direction. On the other hand, the second electrode **17** of the cold cathode

electron emitter is composed of an array of second electrode strips **Y1** to **Y8**, which are arranged to be spaced from each other in a direction intersecting with said lateral direction. Therefore, the strong field drift layer **12** is disposed between the array of first electrode strips **X1** to **X8** and the array of second electrode strips **Y1** to **Y8**.

In this case, when the voltage is applied between at least one of the first electrode strips **X1** to **X8** and at least one of the second electrode strips **Y1** to **Y8** by the voltage applying unit, the electrons are selectively emitted from an intersecting region(s) therebetween. For example, as shown in FIG. 18A, when the voltage is applied between the first electrode strips **X1**, **X2** and the second electrode strips **Y2, Y3**, electrons are emitted from the intersecting region **R1**. In addition, when the voltage is applied between the first electrode strips **X4, X6** and the second electrode strips **Y4, Y6**, electrons are emitted from plural intersecting regions **R2**. Thus, the modifying apparatus of this embodiment is suitable to efficiently perform the modifying treatment to the object having regions, which the irradiation of electrons is not needed. In addition, there is an advantage of saving power consumption.

To readily change the electron irradiation area, it is preferred that the modifying apparatus further comprises a first selector for selecting at least one of the first electrode strips **X1** to **X8**, and a second selector for selecting at least one of the second electrode strips **Y1** to **Y8**, and a controller for controlling the voltage applying unit in response to outputs of the first and second selectors. In this case, the controller controls the voltage applying unit such that the voltage is applied between at least one of the first electrode strips **X1** to **X8** selected by the first selector and at least one of the second electrode strips **Y1** to **Y8** selected by the second selector to selectively generate the electrons from the intersecting region(s) therebetween.

(FIFTH EMBODIMENT)

This embodiment explains about a modifying treatment performed under a condition that an object **2** directly contacts an electron emitting portion **10** of

the cold cathode electron emitter **1**.

As shown in FIG. 19, the object **2** is directly placed on an electron emitting surface of the cold cathode electron emitter, and then electrons are irradiated to the object by the cold cathode electron emitter. In this case, as compared with a case that the object is spaced from the cold cathode electron emitter by a required distance, it is possible to minimize interference between the electrons emitted from the cold cathode electron emitter and atoms or molecules existing in the space therebetween. As a result, variations in energy distribution of electrons irradiated to the object can be reduced to uniformly perform the modifying treatment.

In addition, it is preferred that the whole object **2** is positioned in an electron penetrating region **Rp**, which is defined over a distance in a normal direction to the electron emitting surface of the cold cathode electron emitter **1**. The distance is determined such that the electrons emitted from the cold cathode electron emitter **1** can pass through the object **2** placed in the electron penetrating region **Rp**. For example, when the object is a liquid or solid, it is preferred that the distance is smaller than 1 mm. In addition, when the object is a gas, it is preferred that the distance is smaller than 10 cm. As described below, this method is useful to activate the inside as well as the surface of the object by the irradiation of electrons.

As shown in FIG. 20, the object **2** made of a catalyst material is disposed on the cold cathode electron emitter **1** such that a bottom surface of the object directly contacts the electron emitting surface thereof. On the other hand, the top surface of the object is exposed to a gas flow channel **70**. Electrons are emitted to the object **2** by cold cathode electron emitter **1** to activate the catalyst material. When a polluted gas such as exhaust gas is supplied into the gas flow channel **70** by a gas supply unit **72**, it is cleaned by the activated catalyst material. This method can be also utilized to generate hydrogen from methanol or methane. In place of the catalyst material, a biomaterial, or a polymer membrane may be used as the object **2**.

In the above embodiments, a Metal-Insulator-Metal (MIM) electron emitter or a Metal-Insulator-Semiconductor (MIS) electron emitter may be used as the cold cathode electron emitter in place of the Ballistic electron Surface-emitting Device (BSD).

In addition, the apparatus explained in each of the above embodiments can be regarded as the minimum unit in the case of constructing a high performance modifying apparatus, which has the capability of providing a further improved treatment efficiency. For example, such a high performance apparatus can be obtained by forming a two- or three-dimensional array of a plurality of modifying apparatuses, each of which is substantially the same as the apparatus of any one of the above embodiments, such that object is exposed to larger amounts of electrons provided from different directions.

In addition, the modifying apparatus according to any one of the above embodiments may comprise a sensor for detecting the presence or absence of the object in the treatment space, and a switching device(s) for applying the voltage between the first and second electrodes and if necessary between the accelerating electrode and the first electrode in accordance with an output of this sensor. Moreover, the switching device(s) may be operated according to the output of another sensor for detecting information such as amounts or the number of the object(s), posture or position of the object, or the kind of the object. Furthermore, the modifying apparatus may comprise means for controlling parameters such as irradiation amount, irradiation time, and irradiation angle as well as the energy level of electrons, thereby improving the modifying effect and saving power consumption

<Examples>

Some examples of demonstrating modifying effects achieved by use of the modifying apparatuses described above of the present invention are introduced below.

(Example 1)

In this Example, the modifying apparatus shown in FIG. 10 was used. By

applying 15 V to the cold cathode electron emitter **1**, and 100 V to the accelerating electrode **50**, while supplying oxygen gas into the case **20** through the gas inlet **22** under atmospheric pressure, negative ions of oxygen were ejected outside through the opening **21** without the occurrence of ozone. By use of the generated negative ions of oxygen, a refreshing effect to the human body and a propagation of good bacteria such as yeast and acidophilus were confirmed. This effect can be also utilized to propagate a Bacterium coli carrying a useful gene in biological and medical fields.

(Example 2)

In this Example, the modifying apparatus shown in FIG. 11 was used. By applying 15 V to the cold cathode electron emitter **1**, 100 V to the accelerating electrode **50**, and 300 V between the auxiliary electrodes (**55**, **56**), while supplying oxygen gas into the case **20** through the gas inlet **22** under atmospheric pressure, negative ions of oxygen were ejected outside through the opening **21** without the occurrence of ozone. In this case, amounts of the generated negative ions were larger than the amounts generated in Example 1. By use of the generated negative ions of oxygen, a refreshing effect to the human body and a further increase in propagation of good bacteria were confirmed.

(Example 3)

In this Example, the modifying apparatus shown in FIG. 15 was used. By applying 15 V to the cold cathode electron emitter **1**, 500 V to the accelerating electrode **50**, and 300 V to the auxiliary electrode **55**, while supplying a dry air into the case **20** through the gas inlet **22**, and flowing a gas including steam provided from the gas supply unit **72** in the gas flow channel **70** under atmospheric pressure, negative ions of oxygen and minus ion clusters each having an aggregation of water molecules with a diameter of 10 to 20 nm as a nucleus were ejected without the occurrence of ozone from a gas outlet the gas flow channel **70** provided at the side opposed to the gas supply unit **72**. By use of the generated negative ions of oxygen and the minus ion clusters,

antifungal action, antibacterial action, and inactivation of pollen were confirmed. In addition, the indoor air was deodorized and cleaned.

(Example 4)

In this Example, the modifying apparatus shown in FIG. 13 was used. By applying 15 V to the cold cathode electron emitter **1**, 1000 V to the accelerating electrode **50**, and 300 V to the auxiliary electrode **55**, while supplying a dry air into the case **20** through the gas inlet **22** under atmospheric pressure, electrons were irradiated to an agar medium carrying Bacterium coli thereon as the object **2** through the opening **21**. As compared with the case of not irradiating electrons, amounts of colonies of Bacterium coli were remarkably decreased by the irradiation of electrons. Thus, a high bactericidal effect was confirmed.

INDUSTRIAL APPLICABILITY

From understood from the above embodiments, according to the present invention, it is possible to uniformly and efficiently perform various kinds of modifying treatments depending on the energy level of electrons irradiated to the object even when the object is in a liquid or gas state other than the solid state, or an organism. In addition, by using the cold cathode electron emitter comprising the pair of electrodes, and the strong field drift layer including nanocrystalline silicon disposed between the electrodes, i.e., the Ballistic electron Surface-emitting Device (BSD), the modifying treatments can be performed under atmospheric pressure.

Therefore, the modifying apparatus and method of the present invention are expected to be used in a large variety of application areas such as smoke neutralizer, air conditioner, humidifier, dehumidifier, cloth drier, dish drier, lavatory drier, fan heater, cleaner, refrigerator, closet, kitchen cabinet, shoe cupboard, bath room, laundry machine, freezer, ice maker, and sterilizer.